

# SCIENCE FOR CERAMIC PRODUCTION

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## POROUS FILTERING CERAMICS BASED ON SILICATE MATERIALS FROM SIBERIA

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Porous ceramics based on wollastonite and zeolite rocks from Siberia are developed with an apparent density of 30–40% and pore size from 80–100 to 20–40 μm, whose strength significantly exceeds that of similar ceramics based on traditional materials.

The continuous deterioration of the environment has stimulated a demand for porous materials, which demand can be satisfied by high-quality permeable ceramics, in particular ceramic filters for water purification, gas emission, sewage, etc. Expansion of this production under current conditions is impossible without expanding the available domestic raw materials and rational use of known high-grade materials, replacing scarce materials by more accessible and inexpensive ones, and use of nontraditional kinds of materials.

The purpose of the present study is to develop multifunctional porous permeable ceramics with increased strength and filterability based on mineral materials from Siberia.

The contemporary level of porous ceramics technology for various filter elements requires application of raw materials that are subdivided into fillers (chamotte, quartz sand, quartzite, porcelain scrap, corundum etc.), binders (kaolin, bentonite, orthophosphoric acid, sodium silicate solution, etc.), and burning-out (coal, lignin, etc.) additives [1].

The compositions in our study were developed using nontraditional materials: wollastonite rocks as the main component (filler) and zeolite-containing rocks as the binding component of ceramic mixtures. The choice of wollastonite rocks was occasioned by the needle-shaped particle habitus, which creates a spatial skeleton made of mutually interwoven needles in a ceramic matrix, thus imparting constancy of size and high strength simultaneously with high porosity to the product.

Wollastonite-bearing rock from the Altai Region (Veselyi ore deposit) is a wollastonite-diopside material (64.8% wollastonite and 26.6% diopside) with insignificant

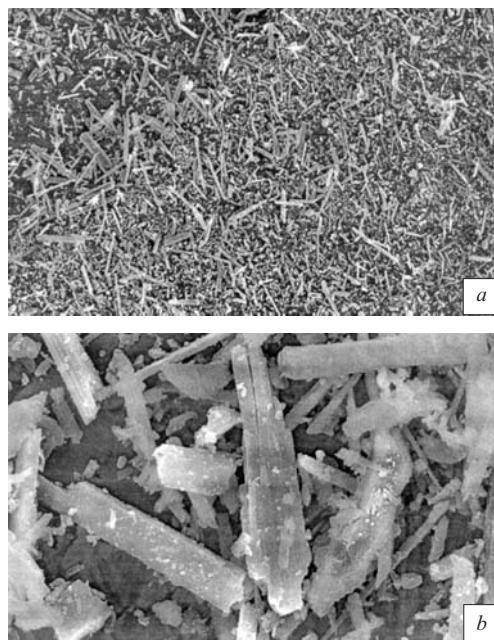
impurities of quartz (3.8%), calcite (3.5%), and magnesite (1.3%). The shape and the size of particles of the rock-forming mineral were estimated using electron microscopy. Samples were prepared by milling the rock until it fully passed through a No. 02 sieve. Microphotos of wollastonite rock samples before and after firing at 1000°C were obtained on a RÉM-100U scanning electron microscope (Figs. 1 and 2).

The microphotos of a nonfired sample exhibit nonisometric needle-shaped particles of proper wollastonite with a needle length from 20 to 200 μm and needle thickness from 2 to 10 μm and prismatic (bar-shaped) particles from 50 to 100 μm long and from 10 to 50 μm thick, which represent non-split packs (aggregates) of needle-shaped wollastonite particles. The presence of isometric particles with a smaller length-to-width ratio is due to the presence of impurity minerals, mostly, diopside. Calcination of wollastonite rock at 1000°C had virtually no effect on the shape and geometric parameters of particles, which confirms that wollastonite is thermally stable up to 1000°C.

The promise of zeolite rocks for producing ceramics is related to their substantial reserves, the proximity of their chemical composition to the composition of many ceramic materials, and to a number of unique properties such as increased resistance to high temperatures, thermal shocks, aggressive media, radioactive radiation, etc.

As for the mineralogical composition, the zeolite-bearing rocks from the Sakhaftinskoe deposit in Krasnoyarsk Region belong to the polymineral type, which is represented by clinoptilolite, heulandite, and mordenite, with prevalence of clinoptilolite. The chemical composition of the rock (Table 1) shows a substantial content of oxides of alkaline and alkaline-earth metals (up to 9.0–9.5%), which determines its fluxing effect in ceramic mixtures. Analysis of the behav-

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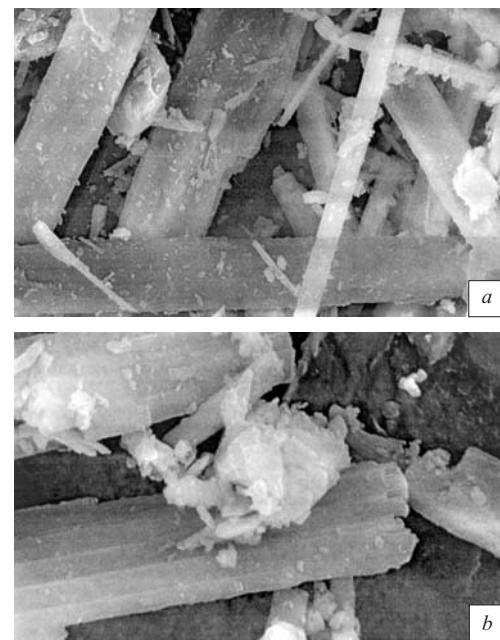
**Fig. 1.** Electron microscope studies of nonfired wollastonite rock at magnification of 230 (*a*) and 2400 (*b*) times.

ior of the rock under heating (derivatography data) identified smooth and continuous dehydration, whereas the main “zeolite” water (around 75% of the total mass of 9.5%) is removed already by 300°C. Dehydration and disintegration of the crystalline structure in zeolite proceeds gradually and not at a specifically registered temperature as in phase transformations. Complete removal of water ends by 700°C. Within the temperature interval of 900 – 1000°C zeolite is seen to become fully amorphous [2].

Zeolite rocks in the present study were tested as a binding component for ceramic mixtures, since after milling they have a certain plasticity and binding capacity in molding, as well as good sinterability in firing [3].

Molding and binding properties were facilitated as well by using the argillaceous rock from the Voronovskoe deposit, which is silty clay that is coarsely dispersed, has a base chemical composition (28.69%  $\text{Al}_2\text{O}_3$ ), a medium content of pigment oxides (1.84%  $\text{Fe}_2\text{O}_3$ ), a hydromica-kaolinite mineralogical composition, and medium plasticity (plasticity number 18.6), is drying-sensitive and high-melting (refractoriness 1520°C), and sinters at medium temperatures (1200°C).

The firing temperature for the mixtures was controlled by introducing an artificial flux in the form of an electric



**Fig. 2.** Electron microscope studies of fired wollastonite rocks at magnification of 2000 (*a*) and 8000 (*b*) times.

bulb cullet, which has an elevated content of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  (17.1%) that makes it effective as a fluxing component; it is also facilitated by a significant content of  $\text{CaO}$  and  $\text{MgO}$  (9.0%) ensuring the formation of low-melting eutectics.

The structure of pore space was developed and controlled in the following way: the mixtures contained a filler (wollastonite rock) of a narrow fraction interval (0.15 – 0.10 and 0.20 – 0.15 mm), a natural binder (argillaceous and zeolite rock), and a burning-out additive, i.e., lignin (5 – 10% above 100%): the binder-to-filler ratio was, respectively, 5 – 50 and 50 – 90%.

Since ceramics with maximum porosity can be produced without special methods of pore formation only from monofractional powders, which in combination with the binder produce loose packing, fillers of various degrees of dispersion were tried: size 0.15 – 0.10 mm in mixtures M1 – M10 and M12 and a larger size 0.20 – 0.15 mm in mixture M11.

The component composition of the mixtures for porous ceramics is listed in Table 2.

Preparations of materials consisted of preliminary crushing and subsequent milling of the binders and nonplastic components to dispersion below 0.5 mm for clay, zeolite, and lignin and below 0.06 mm for glass cullet. Samples were

**TABLE 1**

Component	Mass content, %								
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{BaO}$	$\Delta m_{\text{calc}}$
Clay	58.34	25.85	0.66	1.16	0.76	1.12	0.20	–	9.89
Wollastonite	56.26	1.27	0.39	38.50	5.96	–	–	–	2.66
Zeolite	67.56	11.73	1.98	3.90	0.70	3.57	–	–	10.56
Glass cullet	71.00	0.80	0.10	5.50	3.50	17.10	2.00	–	–

TABLE 2

Mixture	Mass content, %				
	wollastonite (filler)	clay (binder)	zeolite (binder)	cullet (flux)	lignin (burning-out additive)
<i>Wollastonite-argillaceous mixtures</i>					
M1*	90	5	—	5	—
M2*	85	10	—	5	—
M3*	75	20	—	5	—
<i>Wollastonite-zeolite mixtures**</i>					
M4*	50	—	50	—	—
M5*	60	—	40	—	—
M6*	70	—	30	—	—
M7*	50	—	50	5	10
M8*	60	—	40	5	10
M9*	70	—	30	5	10
M10*	50	—	50	5	5
M11***	60	—	40	5	5
M12*	70	—	30	5	5

\* Filler fraction 0.15 – 0.10 mm.

\*\* Cullet and burning-out additive were added above 100%.

\*\*\* Filler fraction 0.20 – 0.15 mm.

molded by semidry molding from molding powders of optimum moisture, which varied depending on the composition from 6.5% (for clay-bearing mixtures) to 9.0% (using zeolite). Molding pressure for each mixture was chosen empirically (the criteria were volume mass and strength of unfired material), which amounted to 5 – 10 MPa.

The optimum firing temperature ensuring the necessary functional properties of porous ceramics was selected by the method of consecutive firing within a temperature interval from 1000 to 1150°C with spacing of 50°C and exposure at the final temperature for 0.5 h.

It was found that use of argillaceous material in mixtures (wollastonite-argillaceous mixtures) in an amount from 5 to 10% has a favorable effect on ceramic properties fired both at 1150°C and at a lower temperature of 1000°C. At the same time satisfactory open porosity (33 – 37%) and strength parameters (25 MPa) of the product are provided. However, in filtering water, a certain part of the filler was washed off, which is undesirable for ceramics used as filters. An attempt to cement the grains of the nonplastic filler in firing by bringing the fraction of the clay component up to 20% (mixture M3) produced an abrupt decrease in the open and through porosity already at 1000°C, due to activated sintering of the disperse system.

A replacement of the argillaceous binder in the mixture by a zeolite binder (wollastonite-zeolite mixtures) in an amount from 30 to 50% (mixtures M4 – M6) under the same firing conditions did not produce the necessary porosity without washing off material. An increase in the firing temperature up to 1150°C led to overburning, as a result of melting of the zeolite component. Consequently, to prevent washing off the finely dispersed fraction and to preserve the porosity level required for filtration in firing within a tempera-

TABLE 3

Parameter*	Mixture			
	M3	M10	M11	M12
Apparent porosity, %	26.0	31.3	41.0	41.6
Apparent density, g/cm <sup>3</sup>	2.06	1.91	1.64	1.70
Pore diameter, μm:				
maximum	46	70	70	64
hydraulic	29	42	36	36
Compression strength, MPa	36.8	27.3	29.5	40.3

\* Firing temperature in all cases was 1100°C.

ture range of 1100 – 1150°C, we varied the ratio between the fluxing (cullet) and the pore-forming (lignin) introduced in respective quantities of 5% and 5 – 10% (mixtures M7 – M12).

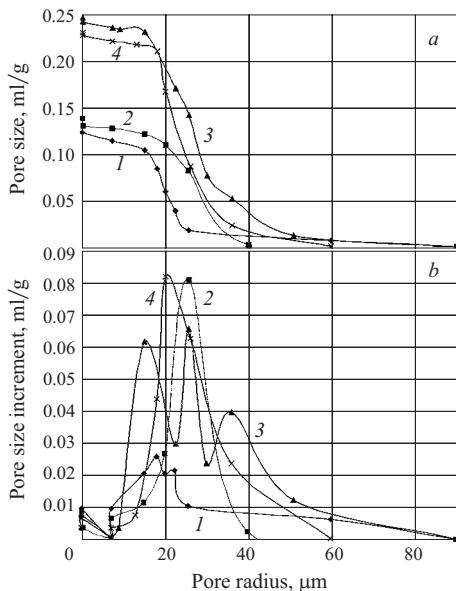
The use of 10% lignin and 5% cullet in mixtures M7 – M9 caused looseness and low cohesion of the product fired up to a temperature of 1150°C. A decrease in the share of the burning-out additive to 5%, while maintaining the ratio of the other components (the filler and the flux) in mixtures M10 – M12, made it possible to completely eliminate material washing off in filtration and to ensure the required level of service properties in products made of these mixtures.

The specifics of the structure synthesized, which was characterized by the pore distribution by sizes in fired material (mercury porosimetry data) and the main properties of samples of the most promising compositions containing argillaceous (M3) and zeolite (M10 – M12) rocks as binders, are listed in Table 3 and in Fig. 3.

It can be seen that samples of mixture M3, which contains up to 20% clay as a binder, have the lowest pore volume compared to other analyzed mixtures. As for the size distribution of pores, the presence of three maxima on the curve for mixture M3 samples (15 – 22, 22 – 25, and 25 – 60 μm) reveals a substantial heterogeneity of structure with prevalence of pores with a radius of 15 – 25 μm. However, there are large pores as well (over 40 – 60 μm).

A partial replacement of clay in the binder component by 50% zeolite rock (mixture M10) makes it possible to obtain articles with a pore volume close to the pore volume of articles based on the clay-bearing mixture M3 but having a homogeneous close-pored structure with pores close in sizes (from 20 to 40%), which is indicated by the existence of only one intense maximum on the pore distribution curve. At the same time, the volume of large (over 60 μm) pores, which play the most significant role for permeability, comprises only 5.0 and 1.5% of the total pore volume in mixtures M3 and M10, respectively.

A decrease in the content of zeolite from 50 to 40% in mixture M11 and the use of a filler of higher dispersion (0.20 – 0.15 mm) is accompanied by an increase in the total porosity. However, similarly to the case of the samples of clay-bearing mixture M3, the pore distribution curve of mixture M11 samples has three maxima in intervals of 10 – 22,



**Fig. 3.** Pore size distribution (*a*) and pore size increment (*b*) in samples of mixtures fired at 1100°C (mercury porosimetry data): 1, 2, 3, and 4) mixtures M3, M10, M11, and M12, respectively.

22 – 30, and 30 – 50  $\mu\text{m}$ , with prevalence of pores with a radius of 22 – 30  $\mu\text{m}$ .

A further decrease in the quantity of zeolite rock from 40 to 30% in mixture M12 together with the use of a the filler of finer fraction (0.15 – 0.10 mm) than in mixtures M11 produces ceramics with a more perfect (homogeneous) structure, a pore volume comparable to the total porosity of samples of mixtures M11, and virtually equal strength parameters.

An interesting correlation exists between the mixture composition and the type of emerging porous structure, which is manifested in monomodality (mixtures M10 and M12) or polymodality (mixture M11) of the pore distribution curves in samples made of these mixtures.

As the structure of a porous ceramic material depends mainly on the packing of the filler particles and their cohesion at contact sides by means of a binder, the use of a finer fraction of the filler (in our case size 0.15 – 0.10 mm) in mixtures M10 and M12 contributes to molding a product with sufficiently fine homogeneous pores, whose initial sizes restrict the possibility of localization of a large volume of the binder inside the pore space, as a consequence of which the structure is formed only by the binder sintering on the filler – binder boundary.

The use of a large filler fraction (0.2 – 0.1 mm) leads to the formation of materials with pores, whose size allows for the presence of a substantial binder volume inside the pores in the molding stage. This binder in subsequent heat treatment sinters inside the volume of a pore as independent fragments and divides it into several pores, which in the case of mixture M11 is manifested in the polymodality of the pore distribution curve. The smallest pores in this case are formed inside the volume of the sintered binder.

Thus, the structure of pore space in porous ceramics can be controlled both by the qualitative and quantitative characteristics of the binding components and by the granulometry of the filler.

Phase formation processes in the considered mixtures were investigated by the x-ray method. The diffraction patterns of clay-bearing mixtures with zeolite binders fired at temperatures of 1100°C and 1150°C are virtually identical; the set of x-ray reflections is the same and differs only in intensity. Qualitatively, the presence of wollastonite is registered in all the analyzed compositions, which is indicated by intense x-ray reflections with interplanar distances at 0.297, 0.352, and 0.218 nm, the presence of diopside with reflections at 0.299, 0.289, and 0.323 nm, and also cristobalite with reflections at 0.404, 0.248, and 0.284 nm and quartz at 0.425, 0.334, and 0.181 nm.

The presence of wollastonite and diopside in the products of firing is related to using wollastonite-diopside rock as the main material for these mixtures, which is evidence of the inert role of wollastonite and diopside proper in coarsely dispersed narrow-fractionated mixtures with argillaceous components in firing up to 1100°C, in contrast to finely dispersed mixtures of clay and wollastonite in which the formation of anorthite is registered as early as 1000°C [4]. The presence of cristobalite is due to the transformation of the impurity quartz component from wollastonite-bearing and argillaceous rocks and the crystallization of amorphous silica as a product of thermal dissociation of argillaceous and zeolite minerals. The role of zeolite and cullet in the phase formation at temperatures of 1100 – 1150°C is reduced to the emergence of an amorphous (vitreous) phase.

The specified porous ceramics developed on the basis of wollastonite and zeolite rocks satisfy the requirements imposed on apparent porosity (30 – 40%) and pore size (from 80 – 100 to 20 – 40  $\mu\text{m}$ ) and significantly exceeds the required strength (30 – 40 MPa against the prescribed 8 – 25 MPa in the case of through permeability) of traditional ceramics intended for similar purposes.

The elevated strength of the porous ceramics is reached due to the needle-shaped habitus of wollastonite particles reinforcing the ceramic matrix and imparting high strength together with high porosity to the material.

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